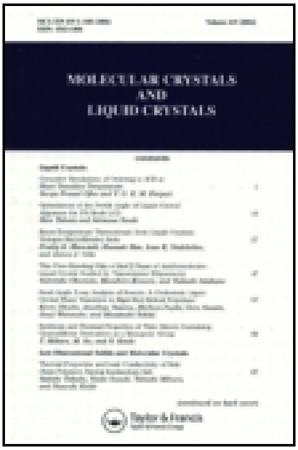

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New Designs for Very High Spin Hydrocarbons

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NEW DESIGNS FOR VERY HIGH SPIN HYDROCARBONS

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Contribution No. 7947

Abstract Several new structures are proposed as tests of a general model for the design of ferromagnetic polymers.

In order to design organic materials with novel magnetic properties, one must be able to control the coupling mechanisms – ferromagnetic or antiferromagnetic – between pairs of spin-containing substructures. Such couplings can be intermolecular, as in the stacking model of McConnell,[1] or intramolecular, as in the very high spin polycarbenes of Itoh, Wasserman, and Iwamura.[2] An understanding , at a fundamental level, of such coupling mechanisms is essential to the development of ferromagnetic materials.

Our own long term goal in this area is the rational design and synthesis of ferromagnetic organic polymers. We see this as a formidable challenge, requiring incorporation into the design of both intramolecular (along the polymer chain) and intermolecular (interchain) ferromagnetic coupling mechanisms. We will describe herein our own thoughts on several aspects of the design problem, and some model compounds intended to test the viability of our options. We emphasize at the outset that we are not alone in the pursuit of ferromagnetic polymers. No doubt other workers have addressed similar issues and perhaps conceived similar models. We are elaborating our approach primarily as a framework for discussion and as a springboard for the design of model systems.

We have conceptually divided the ferromagnetic polymer problem into three smaller objectives. The first is "monomer" design. That is, one needs building blocks with permanent magnetic moments (spin). One then needs to develop ways to link these spins along a polymer so as to ensure ferromagnetic coupling along the chain. Finally, one must ensure that the spin communication among the chains is also ferromagnetic.

The "monomer" problem may not be too severe. Stable organic radicals have been known since 1900, beginning with Gomberg's observation of triphenylmethyl.[3] Various nitroxyls, galvinoxyls, hydrazyls, and related structures are quite stable, commercially available materials. Studies on species such as these have produced a fair amount of insight into the structural features that give rise to stable organic radicals. In contrast, higher spin organic molecules, such as triplets, that are environmentally stable at room temperature are relatively uncommon. Possible examples include several derivatives of the benzene dication with multiple donor substituents that are stable and may have triplet ground states.[1b,f]

The focus of our current efforts is the second stage of design: achieving ferromagnetic coupling along the chain. As schematized in Figure 1, one can conceptually dissect the problem into two components: the spin-containing unit and the ferromagnetic-coupling unit. This is perhaps somewhat arbitrary in that, depending on how one draws the structure, in many systems the spin-containing and ferromagnetic-coupling units can interchange roles. Nevertheless, we have found this approach useful in terms of organizing our thoughts and generating target systems.

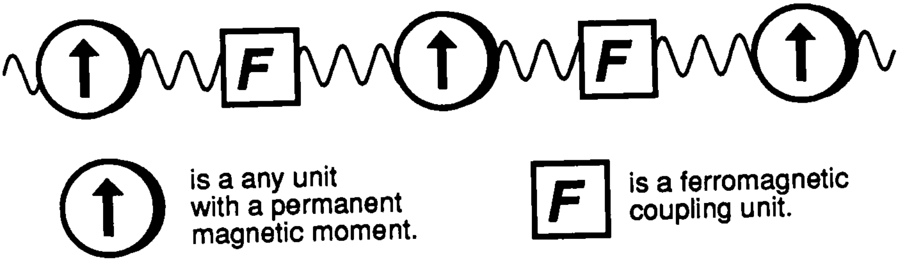

FIGURE 1. An approach to ferromagnetic polymers.

Given the wide variety of spin-containing (monomer) units available, the critical issue is the nature of the ferromagnetic-coupling unit. What organic building blocks ensure a high spin coupling of two spin-containing monomers? Of course, the unit that springs to mind immediately is a benzene ring, *if* the substitution pattern is *meta*. The beautiful and important polycarbene/polynitrene work[2] mentioned above and other studies[4] demonstrate the high-spin coupling of *one-center*, spin-containing structures (carbenes, nitrenes, or simple radicals) *meta* through a benzene (Figure 2). Surprisingly little is known about *meta* coupling other types of spin-containing structures. Since carbenes are likely to be too reactive to produce environmentally stable ferromagnetic polymers, we feel it is important to establish the generality of *meta* coupling as an approach to high spin systems.

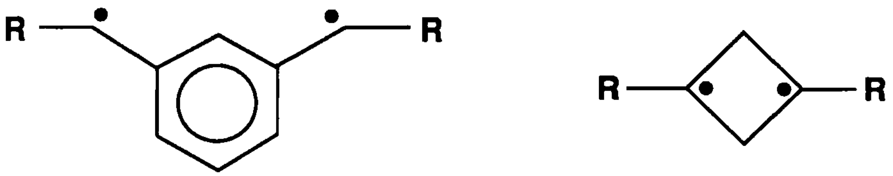

FIGURE 2. Potentially general ferromagnetic coupling units, shown as biradicals for illustration.
left: meta-substituted benzene; right: 1,3 substituted cyclobutane.

Our own work on simple biradicals has suggested a second candidate for a general ferromagnetic coupling unit. We have prepared a variety of cyclobutanediyls and found that all have triplet ground states.[5] We have described such structures as localized biradicals, in that they contain two well-defined radical substructures that are not in classical conjugation with one another. Note that the individual radical units can themselves be delocalized, such as allyl or benzyl. These findings suggest that a 1,3-substituted cyclobutane is also a ferromagnetic coupling unit (Figure 2). They also illustrate what we feel is an important principle: magnetism, unlike, for example, conductivity, does not require fully conjugated (delocalized) π systems. The exchange repulsions that produce ferromagnetic couplings can propagate as easily directly through space (as is the case in the cyclobutanediyls[6]) as along networks of π bonds. Recent work from our labs suggests that 1,3-cyclopentanediyls[7] may also, in general, be triplet ground states. Thus, a 1,3-disubstituted cyclopentane may be another ferromagnetic coupling unit.

A possible advantage of non-delocalizing ferromagnetic coupling units relates to the ultimate material properties of target polymers. Experience from the conducting polymers field indicates that fully planar, conjugated π systems tend to be insoluble, intractable materials. Since a primary reason for preparing a ferromagnetic organic polymer is presumably to combine the magnetic behaviors usually associated with inorganic solids with the favorable material properties of organic polymers, planar π systems may not be attractive final targets. By using a cyclobutane or a cyclopentane as the ferromagnetic coupling unit, one would break the conjugation and introduce some flexibility into the system, which should greatly enhance solubility.

The conducting polymers field also suggests an alternative way around the insolubility problem: the use of soluble prepolymers. The prototype example is the Feast approach to polyacetylene.[8] Given these results, we have chosen polydiazenes (Figure 3) as our ultimate targets. We envision these as stable, processable materials that can be cast into films or other desirable forms. Then, exposure to mild UV irradiation (*ca.* 340 nm) or gentle heating will release N_2 and reveal the high spin structures. This approach also has the advantage that the polydiazene prepolymer can be cooled and/or protected from air prior to N_2 expulsion, should the final polymer require such protections.

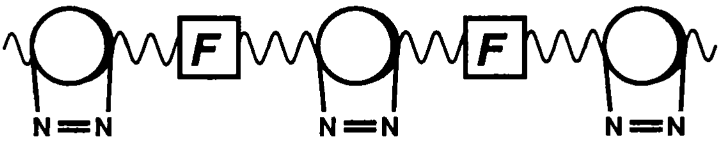

FIGURE 3. Schematic of a polydiazene that could give rise to a structure such as in Figure 1.

Based on these speculations, we have designed and prepared several bisdiazenes intended to test the viability of polydiazenes as precursors to very high spin structures, and the generality of potential ferromagnetic coupling units. These studies also provide valuable tests of our synthetic procedures, as we have learned throughout this work that "bis" chemistry can often be quite different from "mono" chemistry. In particular, we have prepared bisdiazenes **1**, **3**, and **5** as potential precursors of tetraradicals **2**, **4**, and **6**, all of which we would predict to have quintet ground states (Figure 4).

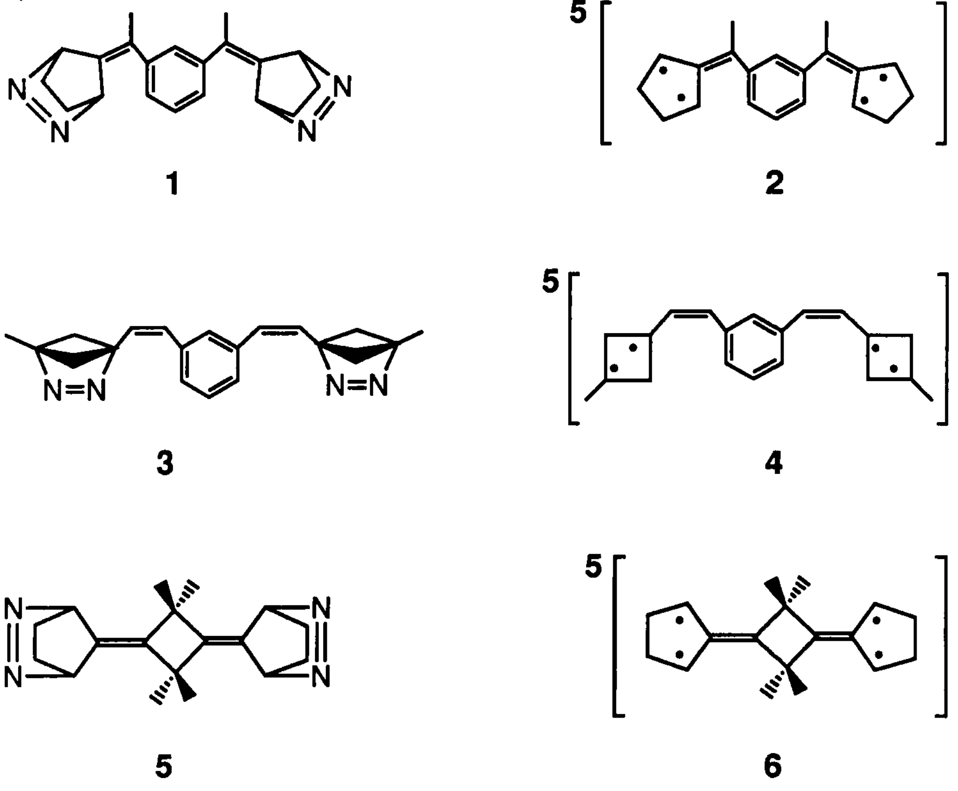

FIGURE 4. Diazene precursors and target quintet molecules for testing ferromagnetic coupling units.

These tetraradicals are assembled from three building blocks: the previously discussed m-xylylene and cyclobutanediyl, and the trimethylenemethane (TMM) derivative 2-alkylidene-1,3-cyclopentanediyl (Berson TMM).[9] TMM's show strong triplet preferences, and incorporation into a five-membered ring renders such structures stable to room temperature, in rigid media. The Berson TMM is thus an excellent spin-containing building block. Tetraradical **2** tests the generality of *meta* coupling as discussed above. It is a fully conjugated π system, and the quintet preference can be anticipated based on a variety of π topology rules.[10]

Structures **4** and **6** are not fully conjugated π systems, and so predictions of spin preferences must be based on more descriptive and, to date, much less tested notions. In **4**, two cyclobutanediyls are coupled through a vinylogous m-xylylene. The double bond spacers are present for synthetic reasons, both for **3** and ultimately for polymers that would be produced by various condensation reactions. Such homologation could "dilute" the spin preferences, and so **4** is an important test. Finally, **6** is composed of two Berson TMM's linked through a cyclobutanediyl. It tests the use of localized ferromagnetic coupling units.

The details of the synthesis of **1**[11], **3**[12], and **5**[13] are described elsewhere. EPR experiments have been carried out on **1** and **5** and we will summarize the results here. Photolysis of **5** at 4 or 77 K in a frozen matrix leads to sequential loss of two equivalents of N_2. The first species seen is an intermediate triplet state that can easily be identified based on its zero field splitting (zfs) parameters as the Berson TMM structure that results from loss of one N_2 from **5**. Further photolysis converts this species to a new structure that displays an EPR spectrum that is readily assignable to quintet **6** based on its zfs values and mode of generation.[13] All available evidence indicates that the quintet is the ground state of **6**, suggesting that cyclobutane could, indeed, be a general ferromagnetic coupling unit.

Similarly, photolysis of **1** at 77 K produces an easily identified triplet Berson TMM due to loss of one N_2. Further photolysis leads to many new EPR transitions. Because of the smaller apparent zfs values, the assignment of these lines to a quintet is more difficult. Our current interpretation is that the quintet of **2** is being produced, although further work will be required to substantiate this assignment.

We consider these results to be quite encouraging, and feel that with further work they will lead to a better understanding of the structural motifs that are best suited to the design of very high spin structures. From these we can proceed to string many spin-containing units together to produce very high spin structures, and then to address interchain high-spin coupling mechanisms.

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